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New Claims: #1-48

This set of claims replaces all previous claims #1-45, submitted with the May 28, 2002 (continued application)

The Old Claims #1-133 of original and consecutive applications are also cancelled and replaced by these current claims

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(new) A process for conducting catalytic reforming of hydrocarbons and alcohols with steam and carbon dioxide for the production of pure hydrogen which includes:

a far outer impermeable hollow tubular cylinder nesting two more concentric permeable tubular cylinders, a next inner and a most inner one, having the most inner permeable cylinder to be nested within the next inner permeable cylinder thus defining three different annular zones including next inner membrane and most inner membrane, with the most inner permeable cylinder to be filled with a reforming catalyst and include gas heating tubes located along the most inner axis, with the catalyst to be in pellet or particle form, with the hydrogen product to be continuously removed via permeation along the most inner membrane wherein the membrane is made by an inorganic or composite material, with the remaining reaction species to partially permeate as well via the most inner membrane, and with the permeated species to be diluted by an inert carrier gas flowing along the next inner annular zone, with hydrogen only to be continuously removed via permeation along the next inner membrane and allow for continuous hydrogen withdrawal out of the most inner catalytic zone and for continuous equilibrium shift of the reactions evolving within this zone, with next inner membrane to be made by a metal or non-porous inorganic material permeable only to hydrogen, with the pure hydrogen to permeate through the next inner membrane and withdrawn along the far outer cylindrical zone.

(new) The process of claim 1 wherein the most inner membrane is made by one or more materials selected from the group consisting of alumina, silica, titania, zirconia,

yttria, and the next inner membrane made by one or more materials selected from the group consisting of aluminum carbide and nitride, silicon carbide and nitride, titanium carbide and nitride, zirconium carbide and nitride, tantalum carbide and nitride, palladium, silver, copper, zinc, tantalum, vanadium, tungsten.

136
3. (new) The process of claim 1 wherein the feed hydrocarbon or alcohol is a single component or a mixture of components selected from the group consisting of methane, ethane, propane, n-butane, i-butane, methanol, ethanol, propanol, butanol, naphtha, gasoline, natural gas, coal gas rich in methane, landfill gas rich in methane, flue gas rich in methane, biomass and sewage gas rich in methane.

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137
4. (new) The process of claim 1 wherein the combined feed hydrocarbon and carbon dioxide gas mixture is selected from the group consisting of a CH_4 and CO_2 mixture, acidic natural gas rich in CH_4 and CO_2, coal gas rich in CH_4 and CO_2, landfill gas rich in CH_4 and CO_2, biomass and sewage gas rich in CH_4 and CO_2, flue and waste gas mixture rich in CH_4 and CO_2.

does it or does it not have steam?

without
138
5. (new) The process of claim 1, 134 with the reject exit stream from the most inner and next inner annular zones is subject to a step which removes steam from the reject exit stream to have the contained steam removed by condensation, and subsequently be passed through a membrane permeator wherein the contained in stream hydrogen and carbon dioxide gases are separated by permeation via a polymer or composite membrane and the non permeated hydrocarbons, alcohols, and/or carbon monoxide exit from the non-permeate side of the permeator as a reject stream, with the

separated hydrogen and carbon dioxide product mixture to be used as a combined fuel-oxidant feed in a molten carbonate fuel cell.

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6. (new) The process of claim 5, wherein the reject stream from the permeator containing each one or a mixture of unreacted hydrocarbons, alcohols, and carbon monoxide is fed in a consecutive steam reforming reaction zone for additional production of hydrogen and carbon dioxide gas products..

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7. (new) The process of claim 5, wherein the reject stream from the permeator containing each one or a mixture of unreacted hydrocarbons, alcohols, and carbon monoxide is recycled into the initial catalytic most inner reforming zone of claim 1 for continuous reforming reaction.

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8. (new) The process of claim 1, with the reject exit stream from the most inner and next inner annular zones is subject to a step which removes steam to have the contained steam removed by condensation and subsequently passed through a cryogenic separator wherein the contained in stream hydrogen and carbon monoxide are separated as gases, while the hydrocarbons, alcohols, and/or and carbon dioxide are separated as condensed liquids and after heating are recycled back into the inlet of the preceding catalytic reforming zone of claim 1 with the separated hydrogen and carbon monoxide product mixture coming from the cryogenic separator to be used in following listed consecutive applications, for fuel gas in solid oxide and molten carbonate fuel cells, for fuel gas in gas turbines and gas engines.

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9. (new) The process of claim 8 wherein the reactant hydrocarbon is methane and the reactant alcohol is methanol.

with the next 143 141

10. (new) The process of claim 8, wherein a part of the separated liquefied hydrocarbons, alcohols, and/or carbon dioxide components from the cryogenic separator are mixed with steam and fed into a subsequent (consecutive) reforming reaction zone for additional production of hydrogen and carbon monoxide which is used in following listed consecutive applications, for fuel gas in solid oxide and molten carbonate fuel cells, for fuel gas in gas turbines and gas engines.

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with the next 144 134

11. (new) The process of claim 1, wherein the reject exit stream consists of hydrogen, carbon monoxide and unreacted steam and enters as a fuel gas feed into a solid oxide or a molten carbonate fuel cell for continuous generation of electricity, with part or all of the permeate hydrogen coming out of the preceding membrane zone to be fed as well in the fuel cell anode inlet in order to provide for supplementary hydrogen fuel feed.

with the next 145 144 wherein a is

12. (new) The process of claim 11 with the flue hot gas emitted by the fuel cell to be used for at least partial heating of the preceding most inner catalytic zone. of claim 1

with the next 146 142 wherein comprises steam and carbon dioxide and/or

13. (new) The process of claim 11 with the flue hot gas emitted by the fuel cell containing steam and carbon dioxide is to be recycled in the inlet of the preceding most inner catalytic zone for use as a reactant in the reforming reaction.

withd. 147 14. (new) The process of claim 134 wherein the permeate hydrogen from the membrane zone is used as fuel feed in a consecutive fuel cell for continuous generation of electricity, with the fuel cell to be one of the listed types: solid oxide, molten carbonate, proton exchange membrane, phosphoric acid, alkaline.

withd. 148 15. (new) The process of claim 147 with the flue hot gas emitted by the fuel cell to be used for at least partial heating of the preceding most inner catalytic zone.

withd. 149 16. (new) The process of claim 147 with the flue hot gas, emitted by the solid oxide and molten carbonate fuel cell, which contains steam and carbon dioxide, to be recycled in the inlet of the preceding most inner catalytic zone for use as a reactant in the reforming reaction.

withd. 150 17. (new) The process of claim 147, wherein the fuel cell is of a cylindrical shape and its fuel anode encloses the cylindrical permreactor in order to receive and consume directly the permeate hydrogen gas as fuel, and with the flue hot gas emitted by the fuel cell to be used for at least partial heating of the encloed most inner catalytic reforming zone.

withd. 151 18. (new) The process of claim 134, wherein the reject exit stream rich in hydrogen, and carbon monoxide after steam condensation is used as fuel feed in a gas engine or gas turbine for continuous generation of electricity, with part or all of the permeate hydrogen coming out of the preceding membrane zone to be fed as well in the engine or turbine in order to provide for supplementary hydrogen fuel.

19. (new) A process for conducting catalytic reforming of hydrocarbons and alcohols with steam and carbon dioxide for production of pure hydrogen which includes:

a far outer impermeable hollow tubular cylinder nesting two more concentric permeable tubular cylinders, a next-inner and a most-inner one, having the most inner permeable cylinder to be nested within the next inner permeable cylinder thus defining three different annular zones including next inner membrane and most inner membrane, with the annular space between the far outer and next-inner cylinders to be filled with a reforming catalyst, with the catalyst to be in pellet or particle form, with hydrogen to be continuously removed via permeation along the next-inner membrane wherein the membrane is made by an inorganic or composite material, with the remaining reaction species to partially permeate as well via the next inner membrane, and with the permeated species to be diluted by an inert carrier gas flowing along the next inner annular zone, with hydrogen only to be continuously removed via permeation along the most inner membrane in order to allow for continuous hydrogen withdrawal out of the far outer catalytic zone and for continuous equilibrium shift of the reactions evolving within this zone, with the most inner membrane to be made by a metal or non-porous inorganic material, and with the permeate pure hydrogen to withdrawn along the most inner cylindrical zone.

20. (new) The process of claim 19 wherein the next inner membrane is made by one or more materials selected from the group consisting of alumina, silica, titania, zirconia, yttria, and the most inner membrane made by one or more materials selected from the group consisting of aluminum carbide and nitride, silicon carbide and nitride, titanium

carbide and nitride, zirconium carbide and nitride, tantalum carbide and nitride, palladium, silver, copper, zinc, tantalum, vanadium, tungsten.

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21. (new) The process of claim 19 wherein the feed hydrocarbon or alcohol is a single component or a mixture of components slected from the group consisting of methane, ethane, propane, n-butane, i-butane, methanol, ethanol, propanol, butanol, naphtha, gasoline, natural gas, coal gas rich in methane, landfill gas rich in methane, flue or waste gas rich in methane, biomass and sewage gas rich in methane.

155 152
22. (new) The process of claim 19 wherein the combined feed hydrocarbon and carbon dioxide gas mixture is selected from the group consisting of a CH_4 and CO_2 mixture, acidic natural gas rich in CH_4 and CO_2, coal gas rich in CH_4 and CO_2, landfill gas rich in CH_4 and CO_2, biomass and sewage gas rich in CH_4 and CO_2, flue and waste gas mixture rich in CH_4 and CO_2.

with 156 152
23. (new) The process of claim 19, with the reject exit stream from the far outer and next inner annular zones to have the contained steam removed by condensation, and subsequently be passed through a membrane permeator wherein the contained in stream hydrogen and carbon dioxide are separated by permeation via a polymer or composite membrane and the non permeated hydrocarbons, alcohols, and carbon monoxide exit from the non-permeate side of the permeator as a reject stream, with the separated hydrogen and carbon dioxide product mixture to be used as a combined fuel-oxidant feed in a molten carbonate fuel cell.

with claim 157 24. (new) The process of claim 156 23, wherein the reject stream from the permeator containing each one or a mixture of unreacted hydrocarbons, alcohols, and carbon monoxide is fed in a consecutive steam reforming reaction zone for additional production of hydrogen and carbon dioxide gas products.

with claim 158 25. (new) The process of claim 156 23, wherein the reject stream from the permeator containing each one or a mixture of unreacted hydrocarbons, alcohols, and carbon monoxide is recycled into the preceding catalytic far outer reforming zone for continuous reforming reaction.

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with claim 159 26. (new) The process of claim 152 19, with the reject exit stream from the far outer and next inner annular zones to have the contained steam removed by condensation and subsequently passed through a cryogenic separator wherein the contained in stream hydrogen and carbon monoxide are separated as gases while the hydrocarbons, alcohols, and carbon dioxide are separated as condensed liquids and after heating are recycled back into the inlet of the preceding catalytic reforming zone, with the separated hydrogen and carbon monoxide product mixture coming from the cryogenic separator to be used in following listed consecutive applications, for fuel gas in solid oxide and molten carbonate fuel cells, for fuel gas in gas turbines and gas engines.

with claim 160 27. (new) The process of claim 159 26 wherein the reactant hydrocarbon is methane and the reactant alcohol is methanol.

withdrawn 28. 161 (new) The process of claim ~~26~~ 158, wherein a part of the separated liquefied hydrocarbons, alcohols, and carbon dioxide components from the cryogenic separator are mixed with steam and fed into a consecutive reforming reaction zone for additional production of hydrogen and carbon monoxide which is used in following listed consecutive applications, for fuel gas in solid oxide and molten carbonate fuel cells, for fuel gas in gas turbines and gas engines.

withdrawn 29. 162 (new) The process of claim ~~19~~ 152, wherein the reject exit stream consists of hydrogen, carbon monoxide, and unreacted steam which enters as a fuel gas feed into a solid oxide or molten carbonate fuel cell for continuous generation of electricity, with part or all of the permeate hydrogen coming out of the preceding membrane zone to be fed as well in the fuel cell anode inlet in order to provide for supplementary hydrogen fuel feed.

with d. 30. 163 (new) The process of claim ~~29~~ 162 with the flue hot gas emitted by the fuel cell to be used for at least partial heating of the preceding far outer catalytic zone.

with d. 31. 164 (new) The process of claim ~~29~~ 162 with the flue hot gas emitted by the fuel cell containing steam and carbon dioxide, to be recycled in the inlet of the preceding far outer catalytic zone for use as a reactant in the reforming reaction.

withd 165 152
32. (new) The process of claim 19 wherein the permeate hydrogen from the membrane zone is used as fuel feed in a consecutive fuel cell for continuous generation of electricity, with the fuel cell to be one of the listed types: solid oxide, molten carbonate, proton exchange membrane, phosphoric acid, alkaline.

withd 166 165
33. (new) The process of claim 32 with the flue hot gas emitted by the fuel cell to be used for at least partial heating of the preceding far outer catalytic zone.

D withd 167 165
34. (new) The process of claim 32 with the flue hot gas containing steam and carbon dioxide, emitted by the solid oxide and molten carbonate fuel cell, to be recycled in the inlet of the preceding far outer catalytic zone for use as a reactant in the reforming reaction.

withdrawn 168 165
35. (new) The process of claim 32, wherein the fuel cell is of a cylindrical shape and its fuel anode encloses the cylindrical permreactor in order to receive and consume directly the permeate hydrogen gas as fuel, and with the flue hot gas emitted by the fuel cell to be used for at least partial heating of the enclosed far outer catalytic reforming zone.

withdrawn 169 152
36. (new) The process of claim 19, wherein the reject exit stream rich in hydrogen, and carbon monoxide after steam condensation is used as fuel feed in a gas engine or gas turbine for continuous generation of electricity, with part or all of the permeate hydrogen coming out of the preceding membrane zone to be fed as well in the engine or turbine in order to provide for supplementary hydrogen fuel.

37. (new) A process for conducting catalytic hydrocarbon reforming with carbon dioxide, for production of pure hydrogen and carbon dioxide which includes:

a far outer impermeable hollow tubular cylinder nesting two more concentric permeable tubular cylinders, a next-inner and a most-inner one, having the most inner permeable cylinder to be nested within the next inner permeable cylinder thus defining three different annular zones including next inner membrane and most inner membrane, with the annular space between the far outer and next-inner cylinders to be filled with a reforming catalyst in pellet or particle form, with hydrogen and carbon dioxide to be continuously removed via permeation along the next-inner membrane wherein the membrane is made by an inorganic or composite material, with the remaining reaction species to partially permeate as well via the next inner membrane and with the permeated species to be diluted by an inert carrier gas flowing along the next inner annular zone, with hydrogen and carbon dioxide species to be continuously removed via permeation along the most inner membrane, with the most inner membrane to be made by a polymer or inorganic material which is permeable to both hydrogen and carbon dioxide species, with the permeated binary hydrogen-carbon dioxide mixture to be withdrawn by flowing along the most inner cylindrical zone.

38. (new) The process of claim 37 wherein the next inner membrane is made by one or more materials selected from the group consisting of alumina, silica, titania, zirconia, yttria, and the most inner membrane made by one or more materials selected from the

group consisting of alumina, silica, titania, zirconia, yttria, polyimides, polycarbonates, polybenziimidazoles, polyphospazenes, polysulfones.

172
~~39.~~ (new) The process of claim 37 wherein the feed hydrocarbon or alcohol is a single component or a mixture of components selected from the group consisting of methane, ethane, propane, n-butane, i-butane, methanol, ethanol, propanol, butanol, naphtha, gasoline, natural gas, coal gas rich in methane, landfill gas rich in methane, flue and waste gas rich in methane, biomass and sewage gas rich in methane.

173
~~40.~~ (new) The process of claim 37 wherein the combined feed hydrocarbon and carbon dioxide gas mixture is selected from the group consisting of a CH_4 and CO_2 mixture, acidic natural gas rich in CH_4 and CO_2, coal gas rich in CH_4 and CO_2, landfill gas rich in CH_4 and CO_2, biomass and sewage gas rich in CH_4 and CO_2, flue and waste gas mixtures rich in CH_4 and CO_2.

withdrawn 174
~~41.~~ (new) The process of claim 172 wherein the combined permeate from the membrane hydrogen and carbon dioxide gas mixture is consumed as fuel-oxidant in a consecutive molten carbonate fuel cell.

withdrawn 175
~~42.~~ (new) The process of claim 174 with the flue hot gas emitted by the molten carbonate fuel cell to be used for at least partial heating of the preceding far outer catalytic zone.

withdrawn 176

43. (new) The process of claim ~~41~~ 174 with the flue hot gas emitted by the molten carbonate fuel cell containing carbon dioxide, to be recycled in the inlet of the preceding far outer catalytic zone for use as reactant in the reforming reaction.

withdrawn 177

44. (new) The process of claim ~~41~~ 174, wherein the molten carbonate fuel cell is of a cylindrical shape and its fuel anode encloses the cylindrical permreactor in order to receive and consume directly as fuel the permeate hydrogen-carbon dioxide mixture, and with the flue hot gas emitted by the fuel cell to be used for at least partial heating of the enclosed far outer catalytic reforming zone.

withd. 178

45. (new) The process of claim ~~37~~ 170 wherein the reject exit stream consisting of hydrogen and carbon monoxide enters as fuel gas feed in the anode of a consecutive solid oxide fuel cell for continuous generation of electricity.

withd. 179

46. (new) The process of claim ~~45~~ 178 with the flue hot gas emitted by the solid oxide fuel cell to be used for at least partial heating of the preceding far outer catalytic zone.

withdrawn 180

47. (new) The process of claim ~~45~~ 178 with the flue hot gas emitted by the solid oxide fuel cell containing carbon dioxide, to be recycled in the inlet of the preceding far outer catalytic zone for use as reactant in the reforming reaction.

withd. 181

48. (new) The process of claim ~~37~~ 170, wherein the reject exit stream rich in hydrogen, and carbon monoxide after steam condensation is used as fuel feed in a gas engine or gas

turbine for continuous generation of electricity, with part or all of the permeate hydrogen and carbon dioxide coming out of the preceding membrane zone to be fed as well in the engine or turbine in order to provide for supplementary hydrogen fuel.